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Brorsson, J., Palmqvist, A., Erhart, P. (2022). Strategic Optimization of the Electronic Transport Properties of Pseudo-Ternary Clathrates. *Advanced Electronic Materials*, 8(3).  
<http://dx.doi.org/10.1002/aelm.202100756>

N.B. When citing this work, cite the original published paper.

# Strategic Optimization of the Electronic Transport Properties of Pseudo-Ternary Clathrates

Joakim Brorsson, Anders E. C. Palmqvist, and Paul Erhart\*

While alloying is a powerful handle for materials engineering, it is an ongoing challenge to navigate the large and complex parameter space of these materials. This applies in particular for thermoelectrics and even more so clathrates. Here, a combination of density functional theory calculations, alloy cluster expansions, Monte Carlo simulations, and Boltzmann transport theory calculations is used to identify compositions that yield high power factors in the pseudo-ternary clathrates  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  and  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$ , while accounting for weight and raw material costs. The results show how a cost-efficient performance can be achieved by reducing the number of Al and Ga atoms per unit cell, while compensating the resulting increase in the carrier concentration via an extrinsic dopant. The approach used in this study is transferable and can be a useful tool for mapping the thermodynamic and transport properties of other multinary systems.

## 1. Introduction

Computationally driven strategies have been demonstrated to accelerate the development of thermoelectrics<sup>[1–10]</sup> as well as other functional materials.<sup>[11–13]</sup> We have previously shown that atomic scale simulations can be used to estimate the physical properties for pseudo-binary type-I clathrates, in spite of the inherently large configuration space.<sup>[14,15]</sup> Here, a similar approach is applied to investigate two even more complex cases, namely the pseudo-ternary systems  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  and  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$ . We focus on thermoelectric performance, since these materials exhibit extremely low thermal conductivities ( $\kappa$ ) together with relatively high electrical conductivities ( $\sigma$ ) and Seebeck coefficients ( $S$ ).<sup>[16–18]</sup> In turn, this leads to a reasonably larger thermoelectric figure of merit  $zT = \sigma S^2 T / \kappa$ , where  $\sigma S^2$  is the power factor (PF).

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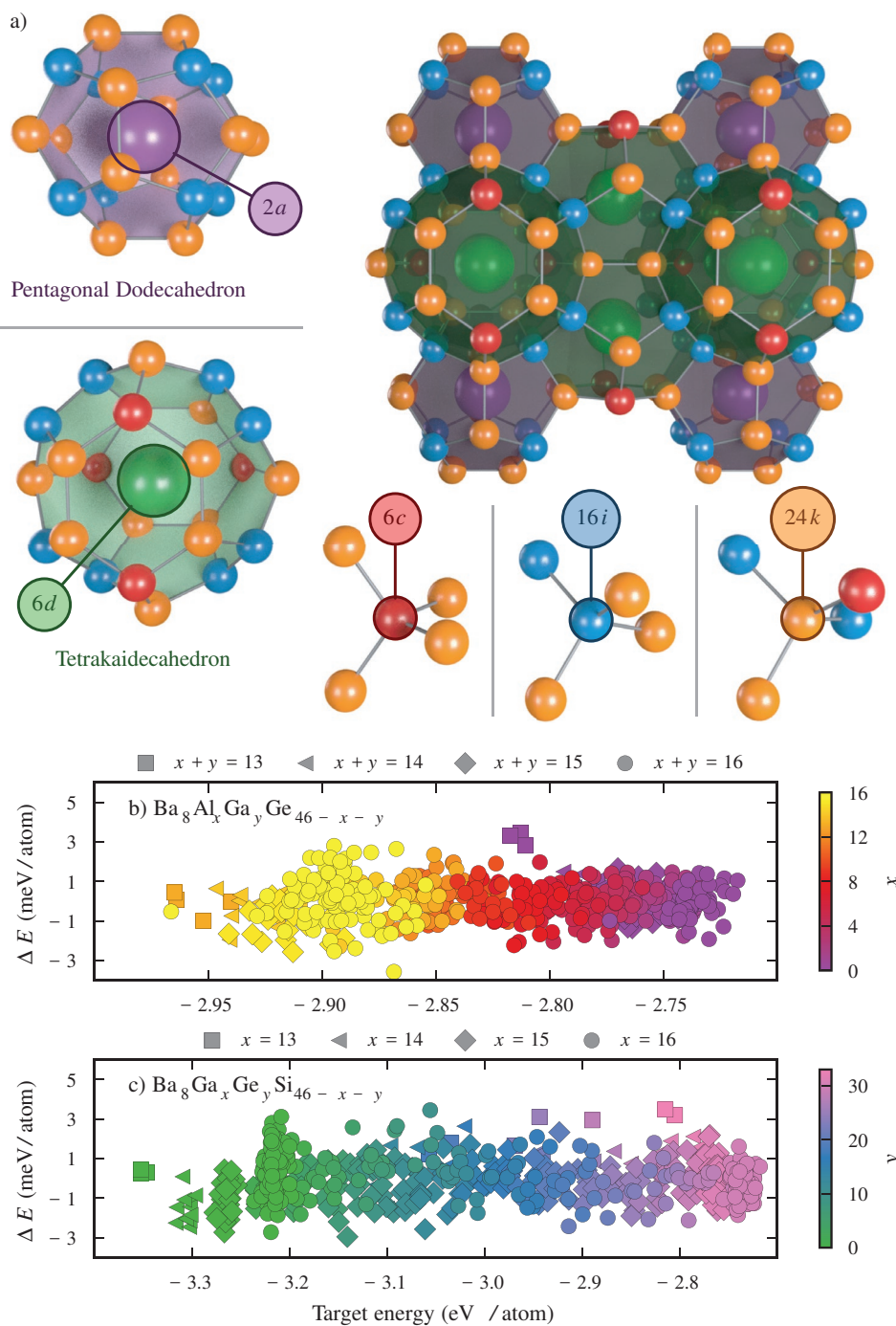
DOI: 10.1002/aelm.202100756

Based on our previous studies of  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ <sup>[14]</sup> and  $\text{Ba}_8\text{Al}_x\text{Ga}_{16-x}\text{Ge}_{30}$ ,<sup>[19]</sup> we know that the electronic transport properties are strongly influenced by chemical ordering, which is a direct consequence of the unique structural motifs of clathrates. They feature a rigid host framework that contains cages which enclose loosely bound guest atoms. Like most studies, our investigation pertains to structures that belong to the type-I subgroup, which possesses  $Pm\bar{3}n$  (International Tables of Crystallography number 223) symmetry and can be described by the chemical formula  $\text{A}_8\text{B}_x\text{C}_{46-x}$ . Here, A represents the guest atoms, which are found at Wyckoff sites 2a and 6d, while the host atoms, B and C, occupy 6c, 16i,

and 24k sites (see Figure 1a). According to the Zintl concept, it is expected that the guest atoms are not directly bonded to the host framework, but rather donate their electrons to the latter so as to ensure that all atoms have a full octet in their valence shell. In  $\text{Ba}_8\text{Al}_x\text{Ga}_{16-x}\text{Ge}_{30}$  and  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_x\text{Si}_{16-x}$ , the 8 pairs of electrons provided by the Ba atoms (+2) are compensated by the relative deficiency (−1) of the 16 trivalent elements (Al, Ga). While both compounds should thus be expected to behave as intrinsic semiconductors, actual samples tend to deviate from the stoichiometric composition, which leads to either a lack (p-type) or surplus (n-type) of electrons.

The Zintl concept alone is, however, not enough to explain the differences in the property measurements that are generally observed, even for samples that have the same nominal composition.<sup>[20–33]</sup> Detailed structural characterisations of different pseudo-binary clathrates have, moreover, revealed that different synthesis methods produce materials with remarkably different site occupation factors (SOFs).<sup>[16,34]</sup> In addition, our previous studies of the pseudo-binaries,  $\text{Ba}_8\text{Ga}_x\text{Ge}_{46-x}$ ,  $\text{Ba}_8\text{Al}_x\text{Ge}_{46-x}$ ,  $\text{Ba}_8\text{Ga}_x\text{Si}_{46-x}$ , and  $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$ <sup>[14,15]</sup> as well as  $\text{Ba}_8\text{Al}_x\text{Ga}_{16-x}\text{Ge}_{30}$ <sup>[35]</sup> have revealed the existence of significant correlations between the electronic transport properties and the degree of chemical ordering. The fact that the latter varies strongly with both temperature and composition, indicates that there exist multiple levers that can be used to tune the thermoelectric performance, especially for pseudo-ternary systems.

It should be emphasized that while the figure of merit of  $\text{Ba}_8\text{Ga}_x\text{Ge}_{46-x}$  can reach values above 1,<sup>[36]</sup> this compound is among the most expensive of all known thermoelectric materials,<sup>[37,38]</sup> which severely limits its viability for practical applications. Since the market prices for Al and Si ( $\approx 2\text{ kg}^{-1}$ )<sup>[39,40]</sup> are substantially lower than Ga ( $\approx 200\text{ kg}^{-1}$ ) and Ge ( $\approx 1000\text{ kg}^{-1}$ ),<sup>[40]</sup>



**Figure 1.** a) Crystal structure of a type-I clathrate.  $6c$  (red),  $16i$  (blue), and  $24k$  (orange) host sites as well as the  $2a$  (purple) and  $6d$  (green) guest sites can be distinguished. (b,c) Prediction errors associated with the b)  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  and c)  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$  CE models.

a potential solution could be to alloy  $\text{Ba}_8\text{Ga}_x\text{Ge}_{46-x}$  with  $\text{Ba}_8\text{Al}_x\text{Ge}_{46-x}$  or  $\text{Ba}_8\text{Ga}_x\text{Si}_{46-x}$ . Another key issue that has been revealed in recent years is that  $\text{Ba}_8\text{Ga}_x\text{Ge}_{46-x}$  has a tendency to decompose, both in air and vacuum, if subjected to high temperatures for prolonged periods of time.<sup>[41]</sup> In this context, the addition of a third framework species could provide entropic stabilization, which is the basic principle behind high-entropy alloys.<sup>[42–44]</sup>

Given these considerations, here, we present a systematic computational study of the thermoelectric PF as a function

of composition in  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  and  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$  in relation to the cost of these compounds. This is accomplished via a combination of density functional theory (DFT) calculations, Monte Carlo (MC) simulations based on cluster expansion (CE) models and Boltzmann transport theory (BTT) calculations. In the next section, we first summarize the CE models and then show evidence for chemical ordering, followed by a detailed discussion of the calculated PFs. Technical information related to the methodology can be found in the supplementary

information, which includes details regarding the DFT calculations (Note S1, Supporting Information),<sup>[45–49]</sup> CE construction (Note S2, Supporting Information)<sup>[50,51]</sup> and sampling via MC simulations, (Note S3, Supporting Information)<sup>[52–54]</sup> as well as the BTT calculations (see Note S4, Supporting Information and Figure S1, Supporting Information).<sup>[55,56]</sup>

## 2. Results and Discussion

### 2.1. Performance of the Cluster Expansions

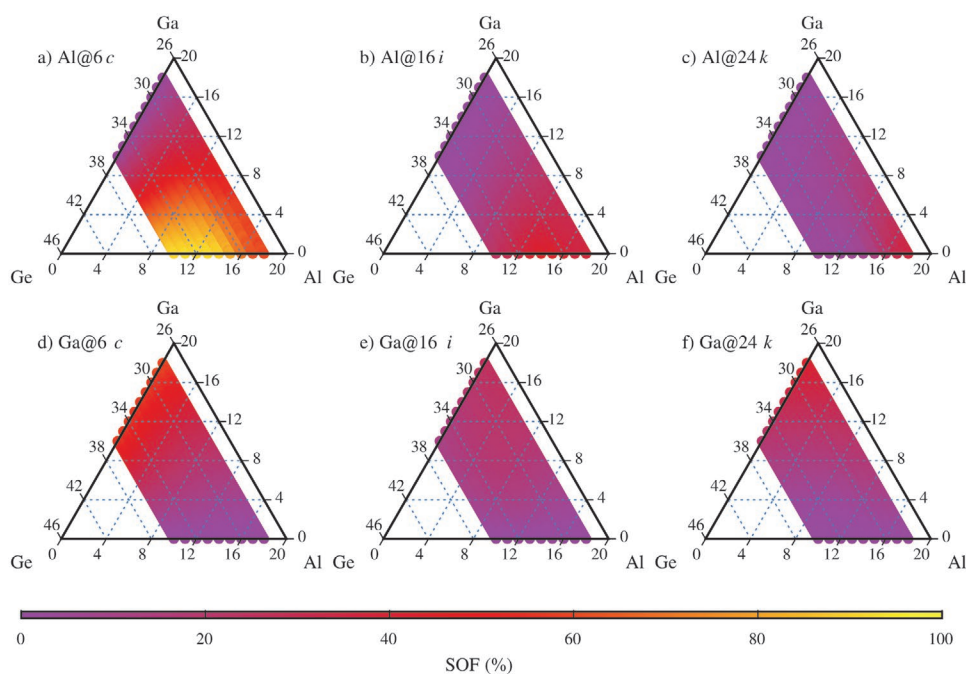
Based on a thorough testing of three alternative fitting methods, we decided to use recursive feature elimination (RFE) with ordinary least squares (OLS) to train the CEs, since it results in low cross-validation (CV) root-mean-square error (RMSE) scores for relatively few non-zero parameters (Figure S2, Supporting Information). The final  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  ( $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$ ) model gave an error of only 1.49 meV site<sup>-1</sup> (0.54 meV site<sup>-1</sup>), when 90% of the available structures were used for training, even though it included just 23 (29) pairs as well as 5 (6) triplets (Figure S3, Supporting Information). As a further measure of the performance of the CEs we calculated the predictive errors for all target energies, which fall between  $\pm 2$  meV atom<sup>-1</sup>. Both the  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  (Figure 1b and  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$  (Figure 1c) CEs are thus comparable in performance to those that we have previously reported for  $\text{Ba}_8\text{Ga}_x\text{Ge}_{46-x}$ ,  $\text{Ba}_8\text{Ga}_x\text{Si}_{46-x}$ ,  $\text{Ba}_8\text{Al}_x\text{Ge}_{46-x}$ , and  $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$ .<sup>[15]</sup> To further validate the models, we compared the SOFs obtained from sampling CEs ensembles, for both pseudo-ternary and pseudo-binary clathrates, with experimental data<sup>[34,35,57–67]</sup> (see Note S5, Supporting Information and Figure S4, Supporting Information). Overall, good agreement is obtained with respect

to the measured data as well as between the pseudo-ternary and pseudo-binary CEs.

### 2.2. Chemical Ordering

By performing MC simulations based on the CEs, we mapped out the SOFs at 700 K across a large portion of the pseudo-ternary compositional space. To this end, we employed a hybrid method, which involves randomly switching between a canonical and a variance constrained semi-grand canonical (VCSGC) ensemble, to sample all  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  (Figure 2) and  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$  (Figure S5, Supporting Information) configurations with between 6 and 20 trivalent elements (Al and Ga). This approach enabled us to sample a continuous range of compositions while at the same time ensuring that the end points are included (Figure S6, Supporting Information).

The SOF data show that Al has a much stronger tendency to occupy the 6c site, and to a lesser extent 24k, compared to Ga, which leads to a pronounced asymmetry in the  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  system. Such clear trends are not observed in  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$ , although there are slight preferences for Ge and Si to occupy 24k and 16i sites, respectively. These observations can be partially explained by the differences between effective cluster interactions (ECI) singlets, which in the case of  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  (Figure S3, Supporting Information a–c) are more positive for Ga compared to Al and only negative for Ge. For  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$  (Figure S3, Supporting Information f–h), meanwhile, Si provides a larger negative contribution than Ge while the term associated with Ga is positive. As is verified by counting the number of nearest neighbors (Figure S7, Supporting Information), we can also conclude that the strong preference for the 6c site exhibited by Al confirms that



**Figure 2.** Maps of a–c) Al and d–f) Ga SOFs at the 6c (a, d), 16i (b, e), and 24k (c, f) sites for  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$ , obtained from MC simulations at 700 K.



Al–Al and Al–Ga bonds are less favorable than Ga–Ga bonds as expected.<sup>[16]</sup>

### 2.3. Mapping of the Power Factor

While the previously described chemical ordering is interesting in its own right, and a key to understanding the complex chemistry of clathrate compounds, other physical properties are of interest depending on the intended application. Here, we focus on the thermoelectric performance and in particular the PF, which is the product of the electrical conductivity and the square of the Seebeck coefficient ( $S^2$ ). We consider the PF rather than the thermoelectric figure-of-merit  $zT$  since the latter involves the lattice thermal conductivity. The lattice thermal conductivity is intrinsically low in these compounds<sup>[18]</sup> and is dominated by phonon-phonon scattering at the temperatures of interest, which means that further reductions are not only difficult to achieve, but also less effective.<sup>[68]</sup> As the calculation of the lattice thermal conductivity is also computationally orders of magnitude more expensive, we therefore limit ourselves to the PF.

Pseudo-ternary systems, such as  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  and  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$ , are especially interesting with regard to tuning the electric transport properties since they offer the possibility to affect the band structure via the Al/Ga and Si/Ge ratios, respectively, while maintaining nearly the same carrier concentration, which is achieved by fixing the number of trivalent elements (Al and Ga). Our simulations are designed to determine if it is possible to retain or even enhance the PF when substituting Ga and Ge with more earth abundant and inexpensive Al and Si.

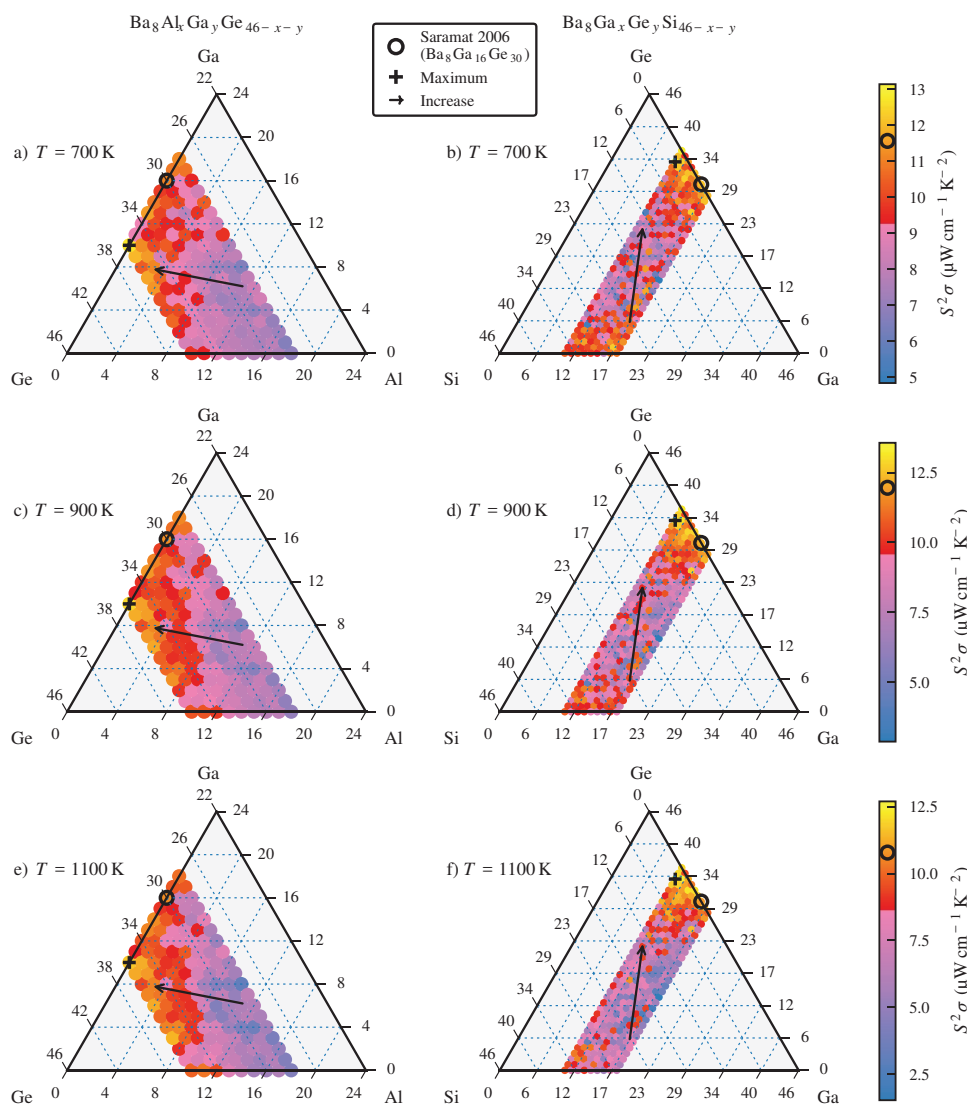
As a reference we have chosen the single crystal sample (disk 15) produced by Saramat et al.,<sup>[36]</sup> which displays a  $zT$  of 1.24 at 1000 K. Since this is one of the highest values reported for any clathrate, it seems likely that the PF must be close to the optimum. For this reason, and because one cannot expect perfect agreement between calculations and measurements, we deem all compositions that correspond to a PF higher than 80% to be of possible interest. Moreover, it is assumed that carrier concentration and relaxation time, which is assumed to be given by the expression  $\tau_{\text{eff}} = \tau_{300\text{K}}(300\text{K}/T)^a$ , are the same for all compositions (see ref. [14] for details). Specifically, the corresponding parameters were selected to achieve agreement with the experimental data reported by Saramat et al.<sup>[36]</sup> for a single crystalline sample (disk 15) of  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  (see Note S4, Supporting Information and Figure S1, Supporting Information). In practice, this means that some type of extrinsic dopant would need to be introduced to compensate for the fact that deviations from the stoichiometric condition, that is 16 trivalent elements, lead to electron excess (Al/Ga < 16) or deficiency (Al/Ga > 16).

Our calculations show that a reduction in the number of Al and Ga atoms generally results in an increase in the PF (Figure 3). Moreover, it is clear that this trend is persistent even when the temperature changes, which means that in further studies it can be sufficient to consider a handful or even just a single temperature. Though mixing of  $\text{Ba}_8\text{Ga}_x\text{Ge}_{46-x}$  with either  $\text{Ba}_8\text{Al}_x\text{Ge}_{46-x}$  (Figure 3a,c,e) or  $\text{Ba}_8\text{Ga}_x\text{Si}_{46-x}$  (Figure 3b,d,f) is in many cases detrimental for the performance, it is also evident that an enhancement can in principle be achieved. In this context, one should keep in mind that the experimental meas-

urements reported so far clearly show that  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ , and in particular the sample selected as a reference,<sup>[36]</sup> tends to have superior properties compared to  $\text{Ba}_8\text{Ga}_x\text{Si}_{46-x}$ ,  $\text{Ba}_8\text{Al}_x\text{Ge}_{46-x}$ , and  $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$ .<sup>[18]</sup> This trend is the most obvious for  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  (Figure 3a,c,e) since the compositions close to  $\text{Ba}_8\text{Al}_{16}\text{Ge}_{30}$  and  $\text{Ba}_8\text{Ga}_{10}\text{Ge}_{36}$  exhibit the lowest and highest PFs, respectively. A possible explanation for this trend is the strong preference of Al for 6c sites (Figure 2) together with the fact that the PF of  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ , as we have previously shown,<sup>[14]</sup> is maximal for a hypothetical structure with no trivalent (Ga) atoms on 6c sites. Still, a performance similar to that of  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  is achieved for compositions with up to 8 Al per unit cell, indicating that it might be worthwhile to investigate at least this region in more detail. This especially applies to  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  with  $x \leq 4$  and  $x + y \leq 11$ . The situation is somewhat different for  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$  because the minimum appears in the middle region, that is when  $\text{Ba}_8\text{Ga}_x\text{Ge}_{46-x}$  and  $\text{Ba}_8\text{Ga}_x\text{Si}_{46-x}$  are mixed in equal proportions. Yet there exist multiple compositions across the entire range for which the PF is similar to or even higher than  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ , in particular at 700 K. More precisely, it would be interesting to explore  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$  with  $x + y < 16$  and either  $x \geq 28$  or  $x \leq 2$ .

We have also performed more detailed test calculations for various  $\text{Ba}_8\text{Al}_x\text{Ga}_{16-x}\text{Ge}_{30}$  compositions ( $0 \leq x \leq 16$ ) as a way of assessing the validity of the earlier observations (see Figure S8, Supporting Information and Figure S9, Supporting Information). These were performed using a previously reported procedure<sup>[35]</sup> and not only account for the existence of an order-disorder transition but also include a correction of the band gap. The results show that the structural transformation has a greater impact for some compositions than others and, especially for a higher Al content, can lead to a reduction in the PF at temperatures above the transition ( $\approx 650\text{K}$ ). Another interesting conclusion is that even though the PF for the compositions with 4 and 8 Al atoms would be lower than for  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  for the same carrier concentration, the values become equally high if the doping level is slightly adjusted. This is a key result since we do not account for this possibility when performing the screening calculations, which encompass a much wider composition range. One should also note that the use of a different reference sample, in the form of a different sample (disk 18) extracted from the same single crystal,<sup>[36]</sup> has a significant impact on the predictions (see Figure S8, Supporting Information and Figure S9, Supporting Information). It is evident that the carrier concentration is almost optimal for disk 18 (Figure S9, Supporting Information) but not disk 15 (Figure S8, Supporting Information). Moreover, the PF is generally larger for the high temperature configuration than the ground state above the transition ( $\approx 650\text{K}$ ) for the former sample while the opposite is true for the latter. These results show that it is indeed wise to not be overly restrictive when analyzing the transport calculations. As was explained earlier, we accounted for this fact by introducing a threshold, which has here been set to 75% of the value for the reference, and treated all compositions with a higher or equal value to be of potential interest.

An important aspect to consider in this context is that the replacement of Ga with Al or Ge with Si confers additional benefits, mainly related to the fact that Al and Si are both lighter, significantly more abundant, and cheaper than Ga and Ge. For this reason we also examined the PF after weighting

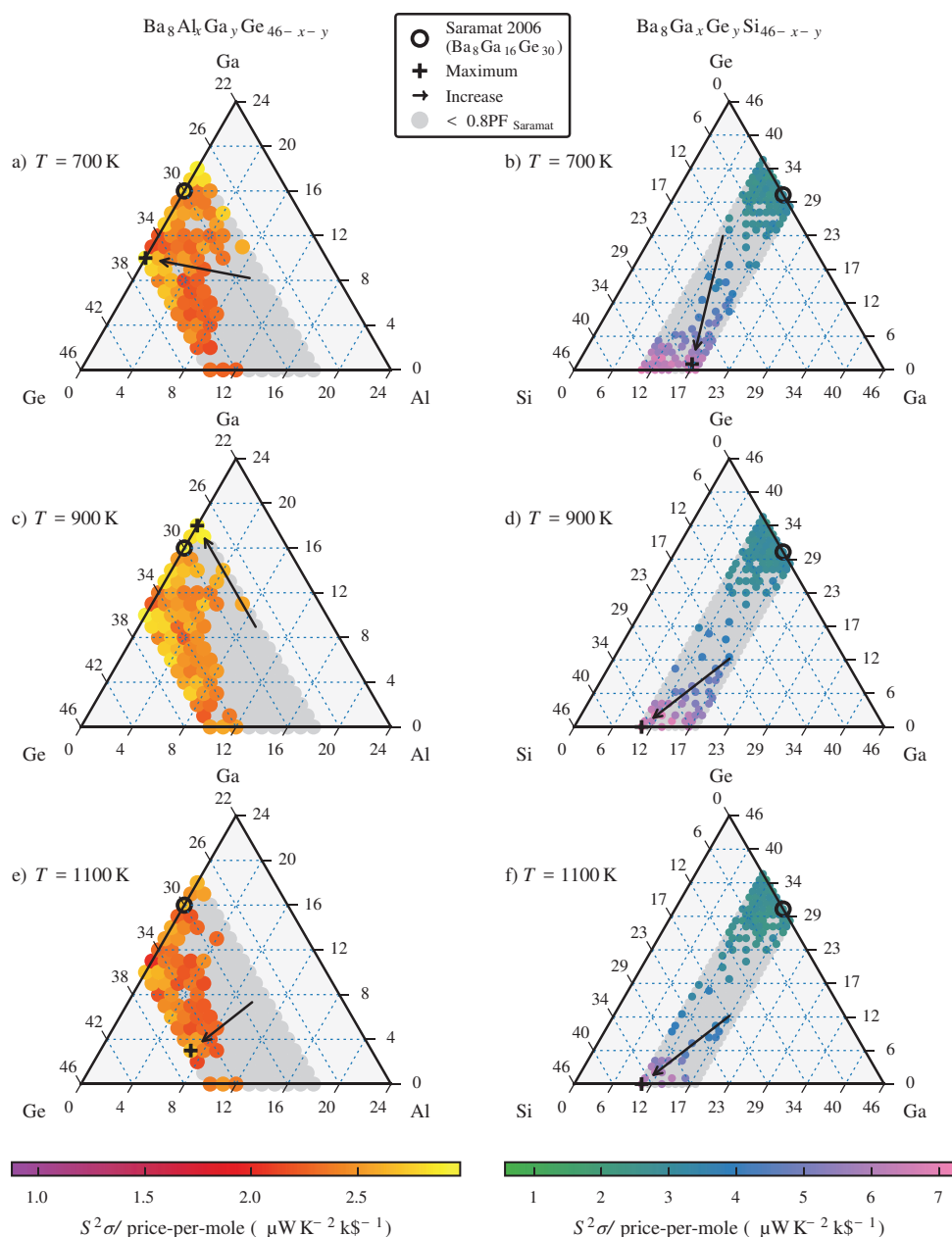


**Figure 3.** Mapping of the PF ( $\sigma^2 S^2$ ) for a,c,e)  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  and b,d,f)  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$  at 700 K (a, b), 900 K (c, d), and 1100 K (e, f). The compositions yielding the maximum PFs (plus sign) as well as the composition of the reference ( $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ , circle) are indicated. The color range for each temperature has been chosen so that the sharp shift (from pink to red) corresponds to 80% of the value predicted for  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ .

it by mass (Figure S10, Supporting Information) and cost (Figure 4) per mole. As should be expected, based on the large difference in mass and market price<sup>[69]</sup> for Al and Si compared with Ga and Ge (see Table S1, Supporting Information and Figure S11, Supporting Information), this shifts the location of the optimum composition, especially in the case of  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$ . This type of analysis further emphasizes that  $\text{Ba}_8\text{Ga}_x\text{Si}_{46-x}$  is expected to be a better alternative than  $\text{Ba}_8\text{Ga}_x\text{Ge}_{46-x}$  for commercial applications. The effect is smaller for  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$ , because Ge is even more expensive than Ga and, additionally, the number of trivalent elements is limited to about 18 atoms per unit cell or lower, which only corresponds to one third of the total number of atoms (54). One should note, however, that this is primarily true at 900 K and 1100 K. At 700 K, inclusion of the cost reduces the variations between the different compositions, which makes it more viable to substitute Ga in  $\text{Ba}_8\text{Ga}_x\text{Ge}_{46-x}$  with Al. It is crucial to emphasize that the

trends outlined above are more pronounced when considering mass (rather than cost), which further enhances the viability of compositions closer to  $\text{Ba}_8\text{Al}_x\text{Ge}_{46-x}$  and  $\text{Ba}_8\text{Ga}_x\text{Si}_{46-x}$ .

In summary, our calculations show that a potential strategy to achieve a high thermoelectric performance for these clathrate systems, is to reduce the number of trivalent elements while at the same time introducing a hole dopant, to compensate for the intrinsic n-doping. Possibly, this could be achieved via a variant of modulation doping, which we have shown to be applicable for the  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  system in its original form,<sup>[70]</sup> where the charge carriers are transferred from the matrix to the doped phase instead of vice versa, which is the conventional idea behind this strategy. Another option is to reduce the number of electrons donated by the guest atoms by partially substituting Ba with an alkali metal such as K<sup>[71]</sup> or Rb. It is also important to note that our calculations of the mixing free energies indicate that it should be possible to mix



**Figure 4.** Mapping of the PF ( $\sigma S^2$ ) weighted by material cost (see Table S1, Supporting Information)<sup>[69]</sup> for a,c,e)  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  and b,d,f)  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$  at 700 k (a, b), 900 k (c, d), and 1100 k (e, f). All compositions that give a power factor lower than 80 % of the value for the reference sample have been uniformly colored (gray). The maximum value (plus) and the reference composition (circle) have also been indicated.

$\text{Ba}_8\text{Ga}_x\text{Ge}_{46-x}$  with  $\text{Ba}_8\text{Ga}_x\text{Si}_{46-x}$  or  $\text{Ba}_8\text{Al}_x\text{Ge}_{46-x}$  in any ratio, provided that the corresponding binaries can be synthesized. The contribution is in fact large enough that the free energy is significantly reduced, suggesting that the mixed system might be less prone to decomposition. Even so, one must keep in mind that all possible phases need to be considered in order to determine thermodynamic stability. Yet there exists substantial experimental evidence that it is indeed possible to produce  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$ <sup>[35,66,70,72]</sup> and  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$ <sup>[64,73,74]</sup> for a wide range of different compositions using a variety of methods. Though these studies have been mainly focused on almost stoichiometric compositions, samples of the corresponding

binary compounds  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ <sup>[20,75,76]</sup>,  $\text{Ba}_8\text{Ga}_{16}\text{Si}_{30}$ <sup>[30,67]</sup> and  $\text{Ba}_8\text{Al}_{16}\text{Ge}_{30}$ <sup>[23,34,77]</sup> have been successfully synthesized that contain either more (only  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  and  $\text{Ba}_8\text{Al}_{16}\text{Ge}_{30}$ ) or significantly less than 16 trivalent elements per unit cell. Consequently, it seems probable that significant portions of the compositional ranges explored in this study could be investigated experimentally.

### 3. Conclusions

In this study, we have used an efficient computational method to map the PFs and SOFs across a large portion of

the configuration space of two pseudo-ternary clathrates,  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  and  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$ . These results show that the presence of Al in  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  leads to a pronounced asymmetry in the SOFs, mainly because it has a much stronger preference for the 6c site compared to Ga, while the variations for Ge and Si in  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$  are almost identical. In agreement with experimental measurements reported so far, our calculations indicate that while improving the electronic transport properties of  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  is not an easy task, there exist multiple  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  and  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$  compositions that are predicted to exhibit a similar, and in a few cases even higher, performance. There are, moreover, indications that this applies in particular if the carrier concentration is optimized for each configuration. Even so, the general tendency is that the substitution of Ga with Al or Ge with Si decreases the PF. Precise control over the stoichiometry and extensive testing is, therefore, likely to be required in order to achieve an enhancement. The situation changes, however, when material weight and cost are taken into account. This is especially apparent in the case of  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$  since compositions close to  $\text{Ba}_8\text{Ga}_x\text{Si}_{46-x}$  are potentially more attractive than  $\text{Ba}_8\text{Ga}_x\text{Ge}_{46-x}$ . Though this effect is less pronounced for  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  it is deemed worthwhile to consider compositions with up to 8 Al atoms per unit cell. For both  $\text{Ba}_8\text{Al}_x\text{Ga}_y\text{Ge}_{46-x-y}$  and  $\text{Ba}_8\text{Ga}_x\text{Ge}_y\text{Si}_{46-x-y}$  however, the maximal PF is achieved by reducing the number of trivalent elements (Al and Ga). Though it might prove difficult to reach the lower limit of the interval examined in this study (Al/Ga = 10), it should be possible to introduce an extrinsic dopant while at the same time decreasing the starting amount of Al and Ga when synthesizing these materials. Lastly, we want to stress that the procedure presented in this paper can, in principle, be applied to any multinary system that displays some degree of chemical ordering. Thus, it can serve as a guide for determining what range of compositions might be the most promising for a certain type of application, which need not be limited to thermoelectrics.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

The authors express their gratitude to Yifei Zhang for many helpful discussions. This work was funded by the Knut and Alice Wallenberg Foundation (2014.0226), the Swedish Research Council (2018-06482, 2020-04935) as well as the Danish Council for Strategic Research via the Programme Commission on Sustainable Energy and Environment through sponsoring of the project "CTEC – Center for Thermoelectric Energy Conversion" (project no. 1305-00002B). The computations were enabled by resources provided by the Swedish National Infrastructure for Computing (SNIC) at NSC, C3SE and PDC partially funded by the Swedish Research Council through grant agreement no. 2018-05973.

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

clathrate, chemical ordering, cluster expansion, Monte Carlo, power factor, transport properties, thermoelectrics

Received: July 26, 2021

Revised: October 28, 2021

Published online:

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